



# EMSP

Environmental Management Science Program

Project Summary Fact Sheet • April 2000



SC-14

## SEPARATIONS CHEMISTRY

### CHEMICAL SEPARATIONS WERE ESSENTIAL FOR WEAPONS PRODUCTION AND THEY ARE ALSO ESSENTIAL FOR COST-EFFECTIVE REMEDIATION

Ion exchangers are most commonly encountered in household water softeners, but removal of very low concentrations of radionuclides in solutions with high salt concentrations presents much more formidable problems. Some EMSP contributions to this important area include:

- Studies of the mechanisms by which crystalline silicotitanates remove cesium from solution.
- New resins for removal of actinides from high-salt waste.
- An inorganic material found to remove over 99.99% of mercury from a dilute solution.

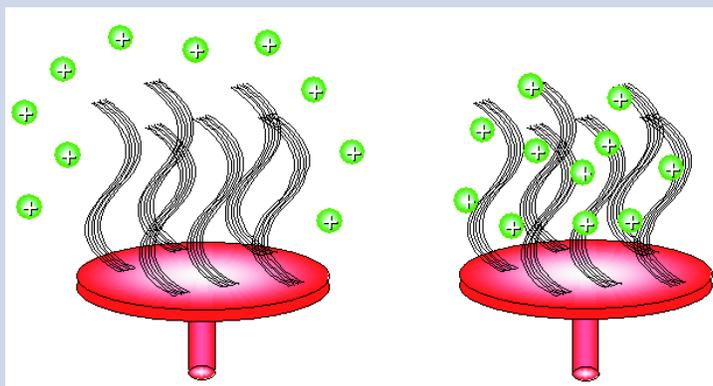
The use of metal-complexing agents or ligands was vital to the separation of the complex mixture produced in plutonium production reactors, and despite the long history of work in this area, new advances in chemistry continually bring opportunities for new applications:

- Some new, large inorganic molecules have been found to sequester certain heavy metal ions in the presence of large excesses of sodium, iron, and aluminum ions.
- New work on a well-known class of organic compounds called crown ethers has resulted in improved selectivity for cesium removal.
- An entirely new class of organic complexing agents was explored for forming metal complexes in a two-step process.

One EMSP project has involved studies of a cyclic reaction as a potential method for the removal of tritium from water. A reaction has been found that proceeds 125 times slower with a tritium-containing compound than for the same compound with hydrogen.

Other EMSP projects include:

- Synthesis of a new form of active carbon for removal of organic compounds from water.
- Studies of chemical processes in supercritical carbon dioxide.



#### Contaminant Removal from Aqueous Streams

This schematic representation from a Northeastern University project (54571) shows the trapping of metal ions from aqueous solution following polarization of an electrically conductive carbon nanofiber electrode.

### PROBLEMS/SOLUTIONS

- The use of some organic complexing agents for removal of metal radionuclides from solution may result in a new mixed-waste disposal problem. An EMSP project has explored the use of a class of inorganic compounds that can remove radionuclides from solution and then be converted into materials suitable for long-term storage.
- The recovery of mercury from solution using organic complexing agents can also result in a new disposal problem. An inorganic material has been found to remove mercury from solution with high efficiency, and metallic mercury can be recovered from the material simply by heating in vacuum.

### ANTICIPATED IMPACT

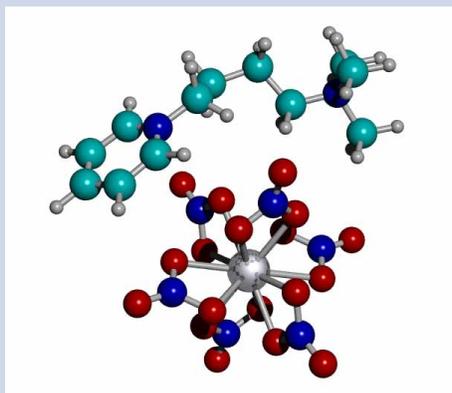
- Needs for improved separation methods are cited by every Focus Area. A few of many examples include cesium, strontium, and technetium separations for pretreatment of Hanford tank waste; transuranic, cesium, and strontium removal from Idaho high activity wastes; removal of radionuclides from Savannah River waste fuel basins; and separation of beryllium from actinides in neutron sources.
- Some of the trisilicates that have been studied by an EMSP project could perhaps be made cheaply enough to be used for groundwater and process water remediation.
- Methods for the removal of tritium from water in tanks, drums, or groundwater have been cited as needed by such diverse sites as the Princeton Plasma Physics Laboratory, Lawrence Livermore National Laboratory, the Hanford Site, the Oak Ridge Reservation, the Savannah River Site, Argonne National Laboratory, and others. An EMSP project has found a remarkable isotope effect on the rates of a simple reaction. While not yet usable as a practical technology, this research may lead the way to a solution to this difficult problem.

## Improved Ion Exchangers

The radioactivity in underground storage tanks is mostly due to cesium-137 and strontium-90. Even though  $^{137}\text{Cs}$  salts are the predominant radioactive species in solutions, the concentration of sodium is at least a million times greater than that of cesium. Crystalline silicotitanate has been extensively studied as an ion exchanger for removal of cesium in tank wastes, and a Texas A&M University/ORNL project (54735) has made detailed studies of the mechanisms by which these and related substances function in order to assist in the design of improved ion exchangers. They have shown how the exchange sites in trisilicates can be designed for most effective cesium removal, and they produced a family of substances using different metal ions. Other substances studied include siderites, sodium micas, zirconia pillared clays, and sodium niobium silicate; these studies involve "crystal engineering" by using various metal ions in the structures to make changes in the crystal geometry, which can cause major changes in selectivity for cesium or strontium.

The LANL/Texas Tech University group (54770) has prepared new mono- and bifunctional anion-exchange resins. They showed that plutonium(IV) in solutions with high nitric acid concentrations could be bound to resins as an anion with six attached nitrates. They developed parameters for molecular modeling studies, which have enabled them to predict optimally arranged anion-exchange sites. A patent has been obtained for the new resins, and the resins have been shown to remove americium(III) from high salt/high acid evaporator waste at LANL. They show promise for small-scale, rapid processing of plutonium scrap.

Lithium-intercalated transition metal disulfides are compounds in which variable amounts of lithium ions are located between layers of metal disulfides that are negatively charged. The Colorado State University group (55012) has prepared such materials with molybdenum disulfide, for example, and finds that they preferentially exchange the lithium ions for heavy metal ions, such as mercury(II) and silver(I) ions. When a solution containing 200 parts per million mercury was treated with a lithium-containing molybdenum disulfide, over 99.99% of the mercury was removed, leaving a solution containing only 6 parts per billion mercury. When the mercury-containing molybdenum disulfide was heated at 425°C under vacuum, near quantitative recovery of metallic mercury was achieved. The starting material could then be regenerated by treating the molybdenum disulfide with an organic lithium compound. Although these materials were found to be effective extractants for heavy metals from aqueous solutions, there was some hydrogen generated by a side reaction. Alternate preparations with a variety of metal sulfides were being investigated to avoid this reaction.



### Improved Ion Exchangers

This computer-generated view provided by a LANL project (54770) shows the 'docking' of the plutonium hexanitrate dianion to a free analogue of the bifunctional dicationic resin site. Models such as this allow determination of the optimal distance between cationic sites for strong ionic binding to specific anions.

## Ionizing-Radiation-Induced Catalysis on Metal Oxide Particles

A new approach for a non-thermal method to destroy organic compounds was investigated by a PNNL project (54996). The idea was to use high-energy gamma radiation to excite an electron in a semiconductor, with the excited electron or hole available for reduction or oxidation chemistry at the surface of the semiconductor. Studies using gamma-irradiation with titanium dioxide,  $\text{TiO}_2$ , particles and oxygen in solution showed a modest increase in reactions of EDTA, but no enhanced reactivities for smaller organic compounds. Extensive surface science studies of model  $\text{TiO}_2$  surfaces under high vacuum conditions have been carried out to understand better at a molecular level how redox processes occur on these surfaces. It was also found that an electron-hole mechanism on semiconductor surfaces is not responsible for decomposition reactions of tetraphenylborate, but rather the formation of benzene occurs by a thermal reaction in the presence of a metal-oxide-supported platinum catalyst as found by other workers at the Savannah River Site.

## New Inorganic Ligand Design

An example of a polyoxometalate is  $\text{NaP}_5\text{W}_{30}\text{O}_{110}^{14-}$ , which is an anion of a water-soluble salt with a sodium ion in a central cavity

surrounded by phosphorous, tungsten, and oxygen atoms. Despite the large size of these compounds, they are made from common oxides and acids. The Georgetown University/ORNL project (54716) is exploring reactions in which a lanthanide or actinide ion may be substituted for the sodium ion in the central cavity. They have found conditions under which neodymium is incorporated in the cavity in the presence of a 200-fold excess of sodium and in the presence of iron and aluminum ions. Several new polytungstate compounds have been made, and the first examples of polytungstate complexes of uranyl,  $\text{UO}_2^{2+}$ , ions have been synthesized. So these radiation-resistant and thermally stable compounds may prove useful for sequestering the radioactive lanthanide and actinide ions for separations from other tank wastes. Also, under relatively mild conditions some of these salts can be converted to cubic bronzes, which contain only actinide or lanthanide, tungsten, and oxygen atoms, and which are being explored as potential waste forms for long-term storage.

## New Organic Ligand Design

The development of new methods for separating or sequestering specific metal ions has been an important part of most industrial processes involving the chemistry of metals. Even though this area has a long history, separation techniques for specific metal ions in the Hanford tanks, for example, still have deficiencies. The design, synthesis, and characterization of improved crown ethers for metal-ion separations are the objectives of the ORNL/ANL/PNNL/University of Tennessee project (55087). The PNNL group has used molecular modeling techniques to attempt to understand the details of sodium or cesium ion binding in order to make suggestions for new compounds that should be investigated. The ORNL group has developed improved syntheses of some previously known crown ether compounds, and guided by the PNNL work, they have prepared a new class of crown ethers with greatly improved cesium to potassium selectivity. The ANL group has explored rational designs of synergistic extraction systems for divalent metals, such as strontium, and they have investigated combinations of acids and crown ethers for solvent extraction systems. The University of Tennessee project has involved attempts to incorporate some of the new crown ethers into polymers in order to prepare resins for use with conventional packed-bed separation systems.

The Washington University project (55223) has also involved molecular modeling techniques for the design of new ligands for metal separations, but their primary focus has been on detailed theoretical computations for some simple metal complexes to obtain a better set of parameters for the molecular modeling programs. They have explored the importance of angular terms in the potentials for metal-ligand interactions, and they intend to validate the force field parameters for various metals by modeling known complexes that were not used in parameter development. Since this work had not been completed at the time of the last report, suggestions for new compounds worthy of experimental study had not yet been made.

The removal of metal ions from dilute solutions requires complexing agents that strongly bind the metal ions. Frequently, however, the rates at which metal ions bind to such ligands are too slow for practical use in separations. The University of Kansas project (54791) has designed molecules that can rapidly form a metal complex and subsequently form a cyclic structure with very tight binding to the metal ion. Even though the first systems studied were chosen to prove the concept, rather than solve specific practical problems, this work demonstrates that such ligands are possible. Another aspect of this project has been the design of imprinted polymers. The idea is to synthesize a polymer in such a way that it will preferentially bind a specific ligand-metal complex. Then if, for example, soil is treated with the ligand to remove a metal, the polymer could be used in turn to remove the complex. The first proof-of-concept studies with a macrocyclic complex for binding of nickel ions suggest that this procedure is feasible.

## Removal of Contaminants from Aqueous Streams Using a New Form of Carbon

Graphite nanofibers have been prepared by the Northeastern University group (54571) using decomposition of hydrocarbons or carbon monoxide over silica-supported metals. They estimate that this material could be produced on a large scale at about a tenth the cost of commercial graphite. It is possible to produce materials where graphite-like platelets are aligned either parallel, perpendicular, or at an angle with respect to the fiber axis. Carbon nanofibers were found to be superior to active carbon in a filter for the removal of organics from water. This material also has a high electrical conductivity and can be used as an electrode in an electrolysis cell. Thus, a metal can be reduced and collected in the porous electrode, and once the nanofibers are saturated with the metal, the contaminant can be discharged into a more concentrated solution by switching the voltage.

## PROJECT TEAMS

### LEAD PRINCIPAL INVESTIGATOR (AWARD NUMBER)

- Northeastern University  
PI: Nelly M. Rodriguez (54571)
- Georgetown University  
PI: Michael T. Pope (54716)  
Oak Ridge National Laboratory
- Texas A&M University  
PI: Abraham Clearfield (54735)  
Oak Ridge National Laboratory
- Los Alamos National Laboratory  
PI: Mary E. Barr (54770)  
Texas Tech University
- University of Kansas  
PI: Daryle H. Busch (54791)
- National Renewable Energy Laboratory  
PI: Daniel M. Blake (54847)
- University of Notre Dame  
PI: Joan F. Brennecke (54942)  
Western Michigan University
- Pacific Northwest National Laboratory  
PI: Michael A. Henderson (54996)
- Colorado State University  
PI: Peter K. Dorhout (55012)
- Oak Ridge National Laboratory  
PI: Bruce A. Moyer (55087)  
Argonne National Laboratory  
Pacific Northwest National Laboratory  
University of Tennessee
- Oak Ridge National Laboratory  
PI: Gilbert M. Brown (55103)  
University of North Carolina
- Washington University  
PI: Garland R. Marshall (55223)



#### Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Many of the current environmental remediation problems in the U.S. Department of Energy (DOE) complex result from using hazardous organic solvents for cleaning and other separations tasks. At temperatures above 31°C and pressures above 78 atmospheres, carbon dioxide, CO<sub>2</sub>, is a supercritical fluid and has been widely studied as a replacement for organic solvents for such tasks as removal of organic compounds from metal surfaces. A project at the National Renewable Energy Laboratory (54847) has investigated photocatalytic methods to oxidize the organic materials once they have been dissolved in the supercritical CO<sub>2</sub>. They have used oxygen in the CO<sub>2</sub> and titanium dioxide catalysts to photooxidize some common organic solvents. Although rates are slower in supercritical CO<sub>2</sub> than in the gas phase, it was demonstrated for the first time that photocatalytic oxidations can be carried out in this medium.

#### Solubility of Metal Complexes in Supercritical Carbon Dioxide

Supercritical carbon dioxide, scCO<sub>2</sub>, has been widely studied and used as a relatively safe solvent for organic compounds. If used with certain complexing agents, then it is also a potentially useful solvent for dissolving a variety of metal salts. The objective of the University of Notre Dame/Western Michigan University project (54942) is to gain a fundamental understanding of the solubility and stability of metal complexes in scCO<sub>2</sub>. They have measured the solubility of some common zinc and iron complexes in scCO<sub>2</sub> and in a mixed solvent with 3% methanol in scCO<sub>2</sub>. They have shown that the solubilities of the metal complexes are increased in the mixed solvent, and spectroscopic studies have revealed that the local environment around the iron complex in solution is enriched in methanol relative to the bulk solution. Ongoing work was concentrating on reliable techniques for phase equilibrium computations.

#### A Cyclic Process for Removal of Tritium from Water

Although the equilibrium properties of different isotopic species are usually very similar, there are some cases in which the rates of chemical reactions are quite different for different isotopes. The ORNL/University of North Carolina project (55103) has investigated the following cyclic process for removal of tritium from water. First, carbon dioxide is electrolytically reduced in water to form the formate ion, HCO<sub>2</sub><sup>-</sup>, where the hydrogen (or tritium) comes from water. Next, a ruthenium(IV) oxo species oxidizes the formate ion back to carbon dioxide. Finally, the ruthenium(II) species produced in the previous step is oxidized electrolytically back to the starting ruthenium(IV) species. The rate constant for the second step was found to be ~300 times greater for the protio-formate ion than for the tritium-containing formate ion, one of the largest kinetic isotope effects ever measured at room temperature. Thus, this cycle would tend to concentrate the tritium in unreacted formate ions, which could be separated by normal ion exchange methods. The kinetic isotope effects for several other reactions were also being investigated.

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**FOR ADDITIONAL INFORMATION ABOUT THE EMSP, PLEASE CONTACT ONE OF THESE REPRESENTATIVES:**

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